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NINTH SEMI-ANNUAL PROGRESS REPORT

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PROCESS MODELLING FOR MATERIALS
PREPARATION EXPERIMENTS

Period of Performance
8/1/93 through 1/31/94

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1. Introduction and General Status

The main goals of the research under this grant consist of the development of mathematical tools and measurement techniques for transport properties necessary for high fidelity modelling of crystal growth from the melt and solution. Of the tasks described in detail in the original proposal, two remain to be worked on:

* development of a spectral code for moving boundary problems,
* development of an expedient diffusivity measurement technique for concentrated and supersaturated solutions.

During this ninth half-year period, good progress has been made on these tasks.

2. MCT Code development

We have focused on developing a code to solve for interface shape, heat and species transport during directional solidification. The work involved the computation of heat, mass and momentum transfer during Bridgman-Stockbarger solidification of compound semiconductors. Domain decomposition techniques and preconditioning methods were used in conjunction with Chebyshev spectral methods to accelerate convergence while retaining the high-order spectral accuracy. As far as we know, this is the first time a Chebyshev pseudospectral method has been applied to a phase-change moving boundary problem. Spectral and pseudospectral methods [1,2] involve the representation of the solution as a truncated series of smooth functions of the independent variables. In contrast to FEM, for which the solution is approximated locally with expansions of local basis functions, spectral methods represent the solution as an expansion in global functions. In this sense they may be viewed as an extension of the separation of variables technique applied to complicated problems [3].

For problems that are characterized either by irregularly shaped domains, or even domains of unknown shape, it is, in general, neither efficient nor advantageous to try to find special sets of spectral functions that are tuned to the particular geometry in consideration (especially in the case of solidification, where the melt-crystal geometry is not known a priori). Two alternative methods are mapping and patching [3]. Mapping allows an irregular region to be mapped into a regular one (which facilitates the use of known spectral functions, such as Chebyshev polynomials). For directional solidification systems the melt-crystal boundary and, thus, the melt and crystal geometries, are unknown. Nevertheless, by specifying the melt-crystal boundary as some unknown single-valued function, the melt and crystal geometries can be mapped into simple ones by a smooth transformation. This mapping facilitates the use of Chebyshev polynomials to approximate the dependent variables in these new domains. Since

heat transfer to and in the ampoule wall as well as in the melt and crystal must also be considered, we employ patching by subdividing the system into four domains (crystal, melt and two ampoule domains), and transform these to domains with simple shapes. We then solve the resulting problems in each domain and solve the full problem by applying suitable continuity conditions across any boundaries (real or artificial) between the computational domains. This includes solving for the melt-crystal boundary shape and location in the untransformed (physical) domain.

The solution algorithm combines Chebyshev pseudospectral collocation, domain decomposition and a finite-difference preconditioned conjugate minimum residual (PCMR) method through a Picard type iterative scheme. This scheme involves four basic steps:

1. The initial shape of the crystal-melt interface is specified. An independent variable transformation is applied to the governing equations and boundary conditions in the melt and crystal regions. This specifies the computational domains.

2. The coupled momentum, heat, mass and species equations are then solved using six of the seven boundary conditions on the moving boundary.

3. The *distinguished* [2] boundary condition (which is not satisfied in the new domain) is used to compute corrected boundary locations.

4. Steps 2 and 3 are repeated until the *distinguished* boundary condition is satisfied.

The code solves equations which describe heat transfer in the ampoule, melt and crystal, and the convective flow problem in the melt. The crystal-melt interface shape is determined as part of the solution. A reprint of the paper [4] describing the results for directional solidification of a single component system is attached to this report. We have subsequently successfully completed an extension of this work to include species transport and the dependence of crystal melting temperature on composition. The solution technique is essentially the same as for the solidification of a pure substance but employs a conjugate-gradient-squared (CGS) technique for the species and heat transport equations, and a preconditioned conjugate minimum residual (PCMR) method for the momentum equations. Finite-difference preconditioning is also employed. The code has been tested extensively against results of Kim and Brown [5] and Adornato and Brown [6] for the directional solidification of mercury cadmium telluride, gallium-doped germanium and silicon-germanium. Further work, beyond these tests, has involved a detailed study of the interplay between convective flow, interface shape and compositional uniformity and includes the dependence of melt density as a non-linear function of temperature and composition. At low CdTe mole fractions ($< 5\%$), this dependence generally exhibits a

density maximum ahead of the solid liquid interface. A manuscript is in preparation that describes the HgCdTe results in detail.

References

[1]   R. Peyret and T.D. Taylor, *Computational Methods for Fluid Flow* (Springer-Verlag, New York, 1983).

[2]   C. Canuto, M. Y. Hussaini, A. Quarteroni and T.A. Zang, *Spectral Methods in Fluid Dynamics* (Springer-Verlag, Berlin, 1988).

[3]   S. Orszag, *Spectral methods for problems in complex geometries*, J. of Computational Physics **37** (1980) 70-92 .

[4]   Y.Q. Zhang and J.I.D. Alexander, *A Chebyshev collocation method for heat transfer, interface shape and convection during directional solidification*, Internat. J. Numerical Methods Heat Fluid Flow **4** (1994) 115-129.

[5]   D.H. Kim and R.A. Brown, *Models for convection and segregation in the growth of HgCdTe by the vertical Bridgman method*, J. Crystal Growth **96** (1989) 609-627.

[6]   P. M. Adornato and R. A. Brown, *Convection and segregation in directional solidification of dilute and non-dilute binary alloys*, J. Crystal Growth **80** (1987) 155-190.

3. Diffusivity Measurement Technique

During the report period we have further improved our experimental setup. These improvements include:

- Temperature control of the measurement cell to 0.1 °C between 10 and 60 °C. This allows for the determination of diffusivities over the whole temperature range of interest for crystal growth from aqueous solutions.

- Enclosure of the optical measurement path outside the ZYGO interferometer in a metal housing that is temperature controlled to the same temperature setting as the measurement cell. This facilitates temperature control of the measurement cell and minimizes distortions of the interferometric image by air flows.

- Simultaneous dispensing and partial removal of the lower concentration (lighter) solution above the higher concentration (heavier) solution through independently motor-driven syringes. In addition, the dispensing and sucking needles, respectively, can be withdrawn with different, predetermined speeds through independent motor drives. This enables the reproducible, experimentor-independent establishment of an initially sharp, flat interface between the two solutions.

- Three-fold increase in data resolution by orientation of the interferometer with respect to diffusion direction.

- Increase of the optical path length in the solution cell to 12 mm. Now 15 interference fringes can be obtained with a 0.05 molar concentration difference between the solutions of a diffusion pair. Compared to our earlier approach, this represents a five-fold increase in the number of fringes at a four-fold reduction in concentration difference. As a consequence, we will be able to determine the concentration-dependence of diffusivities, in particular in supersaturated solutions, with much higher resolution.

During the next reporting period we will add the capability to close the diffusion cell with a lid that contacts the upper solution. This will straighten the solution surface, which is otherwise curved by capillary forces. With this geometrically better defined upper boundary condition we can extend the one-dimenional analysis to diffusion times beyond the point at which the concentration changes reach the upper boundary. Inclusion of this "restricted diffusion" regime in the measurements, in turn, will allow for larger concentration changes between consecutive concentration profiles and, thus further increase in the signal to noise ratio.

4. Presentations and Publications

From the work carried out under this grant the following papers have been published, accepted for publication or are in preparation for submission for publication:

1. A. Nadarajah, F. Rosenberger and J. I. D. Alexander, *Modelling the solution growth of triglycine sulfate in low gravity,* J. Crystal Growth **104** (1990) 218-232.

2. F. Rosenberger, J. I. D. Alexander, A. Nadarajah and J. Ouazzani, *Influence of residual gravity on crystal growth processes,* Microgravity Sci. Technol. **3** (1990) 162-164.

3. J. P. Pulicani and J. Ouazzani, *A Fourier-Chebyshev pseudo-spectral method for solving steady 3-Navier-Stokes and heat equations in cylindrical cavities,* Computers and Fluids **20** (1991) 93.

4. J. P. Pulicani, S. Krukowski, J. I. D. Alexander, J. Ouazzani and F. Rosenberger, *Convection in an asymmetrically heated cylinder,* Int. J. Heat Mass Transfer **35** (1992) 2119.

5. F. Rosenberger, J. I. D. Alexander and W.-Q. Jin, *Gravimetric capillary method for kinematic viscosity measurements,* Rev. Sci. Instr. **63** (192) 269.

6. A. Nadarajah, F. Rosenberger and T. Nyce, *Interferometric technique for diffusivity measurements in (supersaturated) solutions,* J. Phys. Chem (submitted).

7. F. Rosenberger, *Boundary layers in crystal growth, facts and fancy*, in **Studies and Concepts in Crystal Growth,** ed. by H. Komatsu, Progr. Crystal Growth Characteriz. Materials **26** (1993) 87-98.

8. F. Rosenberger, *Short-duration low-gravity experiments - time scales, challenges and results*, Microgravity Sci. Technol. **VI** (1993) 142-148.

9. Y. Zhang, J.I.D. Alexander and J. Ouazzani, *A Chebyshev collocation method for moving boundaries, heat transfer and convection during directional solidification*, Internat. J. Numerical Methods Heat Fluid Flow **4** (1994) 115-129.

10. Konstantin Mazuruk, Ching-Hua Su, Sandor L. Lehoczky and Franz Rosenberger, *Viscosities of molten HgTe and $Hg_{0.8}Cd_{0.2}Te$* , J. Applied Physics (submitted).

11. F. Rosenberger, J. Ouazzani, I. Viohl and N. Buchan, *Physical vapor transport revisited*, J. Crystal Growth (in preparation).

12. J. I. D. Alexander and Y.Q. Zhang, *The density inversion in directionally solidifying HgCdTe melts: Influence on interface shape and convective redistribution of solute* (in preparation).

In addition to the above publications, the results of our work have been presented at the following conferences and institutions:

1. J. I. D. Alexander, *Modelling the solution growth of TGS Crystals in low gravity*, Committee on Space Research (COSPAR) Plenary Meeting, The Hague, Netherlands, June 26 - July 6, 1990.

2. A. Nadarajah, *Modelling the solution growth of TGS Crystals in low gravity* Eighth American Conference on Crystal Growth, Vail, Colorado, July 15-21, 1990.

3. J. I. D. Alexander, *Commercial numerical codes: To use or not to use, is this the question?*, Microgravity Fluids Workshop, Westlake Holiday Inn, Cleveland Ohio, August 7-9, 1990.

4. F. Rosenberger, *Fluid transport in materials processing*, Microgravity Fluids Workshop, Westlake Holiday Inn, Cleveland Ohio, August 7-9, 1990.

5. F. Rosenberger, *Influence of residual gravity on crystal growth processes*, First International Microgravity Congress, Bremen, September 1990 (invited).

6. J. I. D. Alexander, *Residual acceleration effects on low gravity experiments*, Institute de Mechaniques des Fluides de Marseilles, Université de Aix-Marseille III, Marseille, France, January 1991, (3-lecture series, invited).

7. J. I. D. Alexander, *An analysis of the low gravity sensitivity of the Bridgman-Stockbarger technique,* Department of Mechanical Engineering at Clarkson University, April 1991 (invited).

8. A. Nadarajah, *Measuring diffusion coefficients of concentrated solutions,* Fifth Annual Alabama Materials Research Conference, Birmingham September 1991.

9. A. Nadarajah, *Modelling crystal growth under low gravity, Annual* Technical Meeting of the Society of Engineering Science, Gainesville, November 1991.

10. J. I. D. Alexander, *Vibrational convection and transport under low gravity conditions,* Society of Engineering Science 28th Annual Technical Meeting, Gainesville, Florida, November 6-7, 1991.

11. F. Rosenberger, *Theoretical review of crystal growth in space - Motivation and results,* International Symposium on High Tech Materials, Nagoya, Japan, November 6-9, 1991 (plenary lecture, invited).

12. F. Rosenberger, *Computer simulation in materials science,* Mitsubishi Frontiers Research Institute, Tokyo, Japan, November 8, 1991 (invited).

13. F. Rosenberger, *Importance of materials research in space laboratories for industrial development,* International Symposium for Promoting Applications and Capabilities of the Space Environment, Tokyo, Japan, November 14-15, 1991 (plenary lecture, invited).

14. F. Rosenberger, *What can one learn from 10 second low-gravity experiments?,* In Space 1991, Tokyo, Japan, November 14-15, 1991 (plenary lecture invited).

15. P. Larroude, J. Ouazzani and J. I. D. Alexander, *Flow transitions in a 2D directional solidification model,* Sixth Materials Science Symposium, European Space Agency, Brussels, Belgium, 1992 (poster).

16. F. Rosenberger, *Microgravity materials processing and fluid transport,* AIAA Course on Low-Gravity Fluid Dynamics, AIAA Meeting, Reno, NV, January 10-12, 1992 (3-lecture series, invited).

17. J. I. D Alexander, *Numerical simulation of low-g fluid transport,* AIAA Course on Low-Gravity Fluid Mechanics, AIAA Meeting, Reno, NV, January 10-12, 1992 (invited).

18. F. Rosenberger, *Time scales in transport processes and challenges for short-duration low-gravity experiments,* Falltower Days Bremen, Bremen, Germany, June 1-3, 1992 (invited).

19. J. I. D. Alexander, *Modelling or muddling? Analysis of buoyancy effects on transport under low gravity conditions,* World Space Congress, Washington, DC, August 28 - September 5, 1992 (invited).

20. F. Rosenberger, *Modeling of transport in crystallization from vapors*, SIAM Conference on Emerging Issues in Mathematics and Computation from the Materials Sciences, Pittsburgh, PA, April 18-20, 1994 (lecture)

21. J. I. D. Alexander, *Analysis of experiment sensitivity to residual acceleration* International Symposium on Microgravity Science and Application, Beijing, China, May 10-12, 1993 21 (invited).

22. J. I. D. Alexander, *What factors determine the influence of spacecraft attitude motions, vibration and transient disturbances on convective transport in Bridgman systems?* Committee on Space Research (COSPAR), Hamburg, Germany, July 12-16, 1994 (invited).